
पेट्रोलियम के लिए परीक्षण के
तरीके और उसके उत्पाद

[पी : 173]

मोटर गैसोलीन में सीसे की मात्रा ज्ञात
करना — एक्स-रे प्रतिदीप्ति स्पेक्ट्रोमेट्री

Methods of Test for Petroleum
and its Products

[P : 173]

Determination of Lead Content in Motor
Gasoline — Energy Dispersive X-Ray Fluorescence
Spectrometry Method

ICS 75.160.20

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FOREWORD

This Indian Standard [P : 173] was adopted by the Bureau of Indian Standards after the draft finalized by the Methods of Sampling and Test for Petroleum, its Products, Gaseous Fuels and Lubricants Sectional Committee had been approved by the Petroleum, Coal and Related Products Division Council.

This standard elucidates the procedure for determination of lead content in motor gasoline using X-ray Fluorescence Spectrometry (XRF) technique. The detailed calibration analysis in both low range and high range is also described.

While preparing the standard considerable assistance was derived from ASTM D 5059 Standard Test Methods for Lead in Gasoline by X-ray Spectroscopy and IP 352 – 07 “Determination of the lead content of automotive gasoline — Energy-dispersive X-ray fluorescence spectrometry method”.

The use of this standard can involve hazardous materials, operations and equipment. This Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of users of this standard to take appropriate measures to ensure the safety and health of personnel prior to the application of the standard, and to determine the applicability of regulatory limitations and any other restrictions for this purpose.

In reporting the results of a test analysis made in accordance with this standard, if the final Value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 ‘Rules for rounding off numerical values (*revised*)’.

Indian Standard

METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS

[P : 173]

DETERMINATION OF LEAD CONTENT IN MOTOR GASOLINE — ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY METHOD

1 SCOPE

This standard [P : 173] specifies the test procedure for the determination of the lead content of motor gasoline, where the lead is present as lead alkyl. The method is applicable for the lead concentration from 0.002 g Pb/l to 0.50 g Pb/l (low range from 0.002 g Pb/l to 0.020 g Pb/l and high range from 0.01 g Pb/l to 0.50 g Pb/l).

NOTES

- 1 Appropriate calibration plot may be used for different concentration range.
- 2 For samples with higher concentration dilution technique with suitable solvent may be adopted during measurement.
- 3 Oxygenated components of gasoline, such as, alcohols or ethers, may interfere with the results of this method. Differences in density and sulfur content between the product under analysis and the diluent mixture used for the preparation of calibration solutions can lead to errors in the result of the test.

2 REFERENCES

The following standards contain provisions which, through reference in this text, constitute provisions of this standard. All standards are subject to revision, and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below.

<i>IS / ISO No.</i>	<i>Title</i>
1447 (Part 1) : 2000	Petroleum and its products — Methods of sampling: Part 1 Manual sampling (<i>first revision</i>)
ISO 3171 : 1988	Petroleum liquids — Automatic pipeline sampling
17315 (Part 1)/ ISO 4259-1 : 2017	Petroleum and related products — Precision of measurement methods and results: Part 2 Interpretation and application of precision data in relation to methods of test

3 PRINCIPLE

A test portion is exposed to an X-ray beam and the intensity of specified excited lines of lead is measured

and compared with calibration curve of intensity versus lead content. For the high range analysis the intensity of lead L line is measured, whereas for the low range analysis, the low power X-ray tube instrument measures a region of the spectrum centered on the La line together with one set to the high energy backscatter to calculate a net intensity.

NOTE — Calibration and applicable drift correction procedures of the instrument shall be adopted from the instrument manufacturer's guideline.

4 REAGENTS AND MATERIALS

4.1 2,2,4-trimethylpentane (iso-octane) — 99.5 percent minimum purity.

4.2 Toluene — 99.75 percent minimum purity.

4.3 Diluents Mixture — iso-octane and toluene mixed in a proper ratio to match the density of the gasoline under analysis as given in Table 1.

Table 1 Diluents Blend Ratios
(Clause 4.3)

Toluene Percent (V/V)	Iso-octane Percent (V/V)	Density at 15 °C kg/m ³
5	95	705
10	90	714
15	85	723
20	80	731
25	75	740
30	70	749
35	65	758
40	60	766
45	55	775
50	50	784
55	45	793
60	40	802

4.4 Lead Alkyl Compound

Lead alkyl compound with known lead content or Certified Reference Material (CRM) shall be used for preparing the calibration curve.

CAUTION — Contact with lead alkyls may cause adverse and irreversible effects on health. Wear full protective clothing including a face mask and gloves. A separate air supply can also be used. Do not inhale the vapour. Do not allow liquid in contact with skin.

5 APPARATUS

5.1 Energy Dispersive X-Ray Fluorescence Analyzer

CAUTION — Instruments utilizing X-ray sources are to be operated based on manufacturer's safety instructions and local regulations.

5.1.1 An X-ray tube operating at minimum of 25 keV and using suitable targets like palladium, silver, molybdenum, yttrium, rhodium targets have been found to be acceptable (other targets can be used provided that the performance stated in **11.2**, Table 2 is achieved). Instrument operating with sealed radioactive source excitation is also acceptable. However, new generation instruments operating at lower keV and other metallic targets are also suitable as long as its analytical performance and precision matches with the former. Type of detectors, filters and back ground correction techniques of XRF instrument varies. Follow the manufacturer's recommendation and safety instructions.

5.1.2 Model – Sealed Radioactive Source Excitation

5.2 Sample Cells

Cells shall provide a minimum test portion depth of 10 mm and be covered with X-ray transparent film of polyester, polypropylene, polyimide, Mylar or Polycarbonate. Thickness of the film shall be 2.5 micron to 8.0 micron.

5.3 Volumetric Glassware

Class A pipettes, burettes, one-mark volumetric flasks and measuring cylinders as required for the preparation of solutions.

NOTE — All volumetric measurements shall be made at the calibration temperature (normally 20 °C) of the volumetric glassware used ± 2 °C. Deviation from this will lead to inaccurate mass/volume relationships.

5.4 Analytical Balance or Weighing Pipette — Capable of weighing to the nearest 0.1 mg.

5.5 Refrigerator — Suitable for storing flammable liquids that are protected internally to prevent ignition of flammable vapours.

5.6 Water Bath — Controlled at the calibration temperature of the glassware ± 2 °C (*see* **7.1**).

6 SAMPLING

Unless otherwise specified, samples shall be taken by the procedures described in IS 1447 (Part 1) or ISO 3171.

7 PREPARATION OF CALIBRATION STANDARDS

7.1 Stock Solutions of Lead

7.1.1 Stock solution A – High Range (2.00 g Pb/l)

Add 10 ml of lead alkyl compound to 250 ml of the appropriate diluent mixture taken in a 500 ml volumetric flask. Dilute to the mark with diluents mixture and mix thoroughly. Calculate the lead content to the nearest 0.002 g Pb/l. Store stock solutions in a tightly closed dark glass container in refrigerator.

7.1.2 Stock Solution B – Low Range (0.08 g Pb/l)

Add 20 ml of stock solution A to 250 ml of the appropriate diluents mixture taken in a 500 ml volumetric flask. Dilute to the mark with diluents mixture and mix thoroughly. Calculate the exact lead content to the nearest 0.0001 g Pb/l. Store stock solutions in a tightly closed dark glass container in refrigerator.

7.2 Calibration Solutions

7.2.1 High Range Calibration Solutions

With liquids at the glassware calibration temperature ± 2 °C, transfer into successive 100 ml volumetric flasks 0.0 ml, 2.5 ml, 5.0 ml, 10.0 ml, 20.0 ml and 25.0 ml of the stock solution A. Dilute to the mark with the appropriate diluents mixture and mix thoroughly. Calculate the actual lead content to the nearest 0.0001 g Pb/l.

7.2.2 Low Range Calibration Solutions

Follow the procedure in **7.2.1** substituting the unleaded stock solution B for the stock solution A.

NOTE — Certified Reference Materials can also be used for calibration.

8 CALIBRATION

8.1 Calibration for High Range

8.1.1 Spectrometer Settings

Follow the manufacturer's recommendations and set up the X-ray tube voltage, X-ray tube current, primary beam filter, measurement time and multi-channel analyzer region of interest to measure intensity of the L-line X-rays of lead and the K-line X-rays of bromine.

8.1.2 Sample Cell Preparation

Fill a series of sample cells with the high range calibration solutions. Ensure that the depth of solution in each cell is sufficient to make the X-ray count independent of solution depth. Ensure that the film is smooth and flat with no wrinkles or bulges. The cell shall be vented.

CAUTION — Avoid skin contact with the film.

NOTE — Follow the manufacturer's recommendation for ensuring the depth of solution in each cell.

8.1.3 Measurement

Place each cell in the X-ray beam. Measure and record the intensity of the beam under the conditions specified as above. Repeat the measurements using a freshly prepared set of cells.

8.1.4 Line Construction

Use the instrument's regression software to generate the optimum calibration line. The line is normally linear and expressed as:

$$C = A_0 + A_1 R \quad (1)$$

Where

C = is the lead content of the solution, in grams of lead per litre;

A_0 = is the background coefficient;

A_1 = is the sensitivity coefficient; and

R = is the measured X-ray intensity.

8.2 Calibration for Low Range with X-ray Tube

8.2.1 Spectrometer Settings

Set up the X-ray tube voltage, X-ray tube current, primary beam filter, measurement time and two multi-channel analyzer regions of interest, following the manufacturer's recommendations. One is centered on the lead $L\alpha$ line and the other is set to the high energy back-scatter.

NOTE — A typical measurement time is 200 s and may be adjusted as per requirement to ensure necessary precision.

8.2.2 Sample Cell Preparation

Fill a series of sample cells with the low range calibration solutions.

8.2.3 Measurement

Place each cell in the X-ray beam. Measure and record the two intensities for each solution under the conditions specified as above. Repeat the measurements using a freshly prepared set of cells.

8.2.4 Line Construction

Use the instrument's software to convert the readings from each solution into a net intensity of the region of interest around the lead $L\alpha$ line with background removed. Then use the instrument's regression to generate the optimum calibration line. The line is normally linear and expressed by:

$$C = A_0 + A_1 (R_{pb} - F.R_{BS}) \quad (2)$$

Where

C = is the lead content of the solution, in grams of lead per litre;

A_0 = is the background coefficient;

A_1 = is the sensitivity coefficient;

R_{pb} = is the measured intensity of the lead $L\alpha$ line;

R_{BS} = is the measured intensity of the high energy back-scatter; and

F = is the ratio R_{pb} / R_{BS} measured on iso-octane.

8.3 Quality Control

Once daily run a blank (diluent mixture) and any mid-range internal standard on the prepared calibration line. The observed results shall remain within the precision of this method. In case large deviations are observed or desired precision is not met, recalibrate the instrument again.

9 PROCEDURE

Select the procedure to be used for analysis depending upon the anticipated lead content and instrument type. Carry out the measurements as described in the relevant calibration clause. Set the instrument's software to calculate the results from the calibration line in g Pb/l.

10 EXPRESSION OF RESULTS

Report the result to the nearest 0.001 g Pb/l (1 mg Pb/l).

11 PRECISION

The precision was determined by statistical examination by ISO 4259 of inter laboratory test results on gasoline. The precision estimates for reproducibility do not have the same degree of confidence. These estimates are tentative.

11.1 Repeatability

The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the normal and correct operation of the test method, exceed the value given in Table 2 only in one case in twenty.

11.2 Reproducibility

The difference between two test results independently obtained by different operators working in different laboratories on nominally identical test material would, in the normal and correct operation of the test method, exceed the value given in Table 2 only in one case in twenty.

12 RESULT

Report the results of lead content up to third decimal for low range (0.002 g Pb/l to 0.020 g Pb/l) and up to second decimal in case of high range (0.01 g Pb/l to 0.50 g Pb/l).

Table 2 Precision Values
(*Clauses 11.1 and 11.2*)

Procedure	Repeatability g Pb/l	Reproducibility g Pb/l
High range X-ray tube	0.007	0.05815 ($x + 0.2$)b)
High range radioactive source ^{a)}	0.2737 ($x + 0.1$)	0.5539 ($x + 0.1$)
Low range X-ray tube	0.002	0.008b)
Low range radioactive source	N/A	N/A

Where
 x is the average of the results being compared.
 a) value given is for 'premium' grade.
 b) tentative estimate only.

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